I. TERTIARY AMIDES AND HYDROGEN BONDING
II. ENEDIOLS IN THE NAPHTHALENE SERIES

BY

LYELL CHRISTIAN BEHR

B.Chem., University of Minnesota, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS,
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PART I
TERTIARY AMIDES AND HYDROGEN BONDING

INTRODUCTION

Tertiary amides have been studied but little, and those of the higher acids scarcely at all. Primary and secondary amides, being able to serve simultaneously as donors and acceptors, are associated through hydrogen bonds.[1] Tertiary amides are unassociated and, from the standpoint of solubility and basicity, should prove of especial interest in connection with the theory of hydrogen bonding.[2] A number of amides of azelaic and sebacic acids were prepared in order to study the effect of donor properties on the basicity and solubility of these compounds.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The amides were prepared by the reaction of the proper amine (or ammonia) with the acid chloride. *N,N,N′,N′*-Tetramethylsebacamide proved to be a solid which was very soluble in water and most organic solvents. Such high water-solubility was unexpected in view of the high molecular weight of the compound. Sebacamide and its *N,N′*-dimethyl derivative were nearly water-insoluble—this fact is in keeping with the supposed polymeric nature of primary and secondary amides. *N,N,N′,N′*-Tetraethylsebacamide and *N,N,N′,N′*-tetraethylazelamide were liquids which were not very soluble in water, but were readily dissolved by dilute hydrochloric acid. Reprecipitation of the amides could be effected by addition of base. These compounds were very difficult to purify—distillation even at low pressures resulted in decomposition. Hydrochlorides, chloroplatinates, and chloroaurates could be obtained, but only the latter proved suitable for characterization. They were prepared from the amide, auric chloride, and hydrochloric acid, with a little alcohol added, where necessary, to promote solubility of the reactants. The chloroaurates were found to consist of one molecule of the amide combined with one molecule of chloroauric acid.

SUMMARY

1. The following new amides have been prepared: *N,N,N′,N′*-tetramethylsebacamide; *N,N,N′,N′*-tetraethylsebacamide; and *N,N,N′,N′*-tetraethylazelamide.

2. Chloroaurates, chloroplatinates, and hydrochlorides of the compounds have been made.

3. It has been demonstrated that these tertiary amides show basic properties.

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PART II
ENEDIOLS IN THE NAPHTHALENE SERIES

INTRODUCTION

The preparation of the *cis* and *trans* forms of di-(2-methyl-1-naphthyl)-acetylene glycol and some of its derivatives was undertaken in order to compare the stabilizing effect of the 2-methyl-1-naphthyl group with the mesityl,[1] 2,4,6-triethylphenyl,[2] 2,4,6-triisopropylphenyl,[3] 2,6-xylyl,[4] duryl,[5] isoduryl,[5] and other groups.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The starting point in the synthesis of the enediols was 2-methylnaphthalene, which was brominated to give 2-methyl-1-bromonaphthalene. 2-Methyl-1-naphthoic acid resulted when the Grignard reagent was treated with carbon dioxide. It was also obtained, in addition to the amide, by hydrolysis of the nitrile, prepared from the bromo compound, cuprous cyanide, and pyridine.[6] The reaction of excess thionyl chloride on the acid in the cold produced 2-methyl-1-naphthoyl chloride. Treatment of this compound with the binary mixture, magnesium and magnesium iodide, yielded the *cis*-enediol, a white solid which readily underwent auto-oxidation to the deep orange 2,2′-dimethyl-1,1′-naphthil. The presence of solvent, and especially alkalies, accelerated the transformation. Hydrogenation of the diketone in a low-pressure apparatus in the presence of a platinum oxide catalyst produced mainly the *cis*-enediol when the solvent was methanol, and the *trans* isomer when high-boiling petroleum ether was used.

The *cis*-diacetate could be synthesized by heating the *cis*-enediol with acetic anhydride; the *trans*-diacetate was obtained similarly from the *trans*-enediol. In common with other known acetylene glycols, these enediols isomerized to the keto form with comparative difficulty. When *trans*-di-(2-methyl-1-naphthyl)-acetylene glycol was heated with methanol and concentrated hydrochloric acid, the expected 2,2′-dimethyl-1,1′-naphthoin resulted.

Evaluation of the comparative stability of the enediols herein discussed toward oxidation and ketonization is rather difficult, because no quantitative methods of determining these properties are available. A qualitative estimate would place them near the di-(2,4,6-triethylphenyl)-acetylene glycols.

SUMMARY

1. The two forms of di-(2-methyl-1-naphthyl)-acetylene glycol have been prepared.

2. The diacetates of these enediols, 2,2′-dimethyl-1,1′-naphthoin, 2,2′-dimethyl-1,1′-naphthil, and 2-methyl-1-naphthonitrile have been synthesized and characterized.

3. An estimation of the stabilizing effect of the 2-methyl-1-naphthyl group as compared with those in other acetylene glycols has been made.

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VITA

The author was born in Minneapolis, Minnesota, on May 4, 1916. He attended the public schools of that city and matriculated at the University of Minnesota in the fall of 1933. He was graduated in 1937 with the Bachelor of Chemistry degree. He entered the University of Illinois in the fall of the same year as a teaching assistant in organic chemistry, which position he held for three school years and one summer session. He held a University fellowship during 1940-1941. During the summer of 1940 he was employed by the Monsanto Chemical Company.

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